



Low-concentration CO₂ conversion on Ag_xNa_{1-x}TaO₃-AgCl heterojunction photocatalyst

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ABSTRACT

Photocatalytic conversion of low-concentration CO₂ with H₂O oxidation indicates an applicable way to achieve sustainable carbon cycling and solve the global warming problem. Enhancing photogenerated charge separation and surface adsorption and catalytic process of photocatalysts is the crucial point to compensate for the mass transfer limitation during low-concentration CO₂ conversion. Herein, a highly-crystalline Ag_xNa_{1-x}TaO₃-AgCl heterostructure composite was successfully fabricated via a one-step flux method. The *in-situ* formation of intimate heterojunction between Ag_xNa_{1-x}TaO₃ and AgCl facilitated the separation and transfer of photogenerated charges. Moreover, the simultaneous introduction of Ag cations and AgCl components promoted the adsorption and activation of CO₂ on the photocatalyst surface. When combined with metallic Ag cocatalysts, the Ag_xNa_{1-x}TaO₃-AgCl heterostructure photocatalyst exhibited an improved activity for the overall reaction of CO₂ reduction and H₂O oxidation at low CO₂ concentration condition. The design of photocatalysts active at low CO₂ concentration accounts for an alternative way to construct the practical CO₂ conversion system in the future.

1. Introduction

The excessive emission of greenhouse gas CO₂ into the atmosphere has induced continuous global warming, resulting in remarkable climate change together with a series of critical eco-environmental issues [1–4]. The decrease of atmospheric CO₂ concentration and the removal of CO₂ gas from fossil fuel combustion based on carbon capture technologies can effectively prevent the deterioration of the eco-environment caused by the greenhouse effect [5–8]. From the viewpoint of carbon neutrality, it is significant and urgent to utilize CO₂ as a carbon resource to produce value-added fuels and chemicals upon CO₂ capture, which has drawn great attention in the fields of environment protection and energy conversion all over the world [9–11]. In this scenario, solar-driven CO₂ conversion on particulate photocatalysts has emerged as a promising strategy to simultaneously mitigate the increasing environmental problems and achieve sustainable carbon recycling [4,12–14].

Photocatalytic CO₂ conversion using H₂O as the electron donor and proton source is a thermodynamically uphill reaction, which has been regarded as one of the simplest artificial photosynthetic ways towards

future practical application [15–17]. Over the past decades, tremendous efforts have been made to realize one-step excitation photocatalytic CO₂ conversion with H₂O oxidation on ALa₄Ti₄O₁₅ (A = Ca, Sr, and Ba), Zn₂GeO₄, Ga₂O₃, ZnGa₂O₄, KCaSrTa₅O₁₅, NaTaO₃, AgTaO₃, et al [15, 18–23]. The feeding of high-concentration CO₂ gas into an alkaline solution is the necessary mass transfer condition to compensate for the limitation of charge separation and surface catalytic process for these photocatalysts. In consideration of energy depletion for CO₂ gas capture and purification, it is significantly important to investigate the photocatalytic conversion of low-concentration CO₂ with the oxidation of H₂O [24,25]. Perovskite-type NaTaO₃ is a well-known photocatalyst for one-step excitation overall water splitting with the apparent quantum yield reaching 50% at 270 nm [26–28]. Because of its suitable band potential and high charge separation and transfer efficiency, NaTaO₃ has drawn extensive concern in photocatalytic overall reaction of CO₂ reduction and H₂O oxidation [29–31]. Through the generation of surface active sites on NaTaO₃ photocatalyst by doping with Ca, Sr, Ba, or La ion, the photocatalytic activity for CO₂ reduction and H₂O oxidation was dramatically enhanced in comparison with that of pristine NaTaO₃

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[9,22,29–34]. Moreover, the construction of heterojunction structure by combining NaTaO₃ with Ag₃PO₄, Ag₂O or SrTiO₃ is also effective to decrease the recombination of electron-hole pairs, thereby markedly improving the photocatalytic performance [35–37].

In this work, we presented a facile approach for *in-situ* formation of NaTaO₃-AgCl heterostructure together with Ag cation incorporation into NaTaO₃ by the one-step flux method. The suitable band alignment and the intimate interfacial junction of Ag_xNa_{1-x}TaO₃-AgCl composite facilitated the separation of photogenerated charges in the photocatalyst and its high crystallinity with decreased recombination centers promoted the charge carrier transfer efficiency. In addition, the simultaneous introduction of Ag cations and AgCl components provided sufficient active sites for CO₂ adsorption to enhance the surface catalytic process. Owing to the synergistic effect, the Ag_xNa_{1-x}TaO₃-AgCl heterojunction photocatalyst modified with metallic Ag cocatalysts exhibited an impressive performance for the overall reaction of CO₂ reduction and H₂O oxidation at low-concentration CO₂ feeding condition.

2. Experimental section

2.1. Materials

Ag₂O (99%, Innochem, China), NaCl (99%, Innochem, China), Ta₂O₅ (99.99%, Aladdin, China), Na₂CO₃ (99%, Sinopharm, China), AgNO₃ (99%, Sinopharm, China), NaPH₂O₂ (99.99%, Aladdin, China). All chemical reagents were used without further purification.

2.2. Synthesis

2.2.1. Preparation of Ag_xNa_{1-x}TaO₃-AgCl photocatalyst

Ag_xNa_{1-x}TaO₃-AgCl photocatalyst was synthesized by the one-step flux method using Ag₂O, NaCl and Ta₂O₅ as starting materials. The starting materials were mixed in an agate mortar in a ratio of Na: Ta: Ag: Cl = 1: 2: 2: 1. Then excessive NaCl was added as flux. Typically, the solute concentration was defined as a molar ratio of Ag_xNa_{1-x}TaO₃-AgCl to that of the sum of Ag_xNa_{1-x}TaO₃-AgCl and the NaCl flux. The solute concentration was 10 mol%. The mixture was calcined in air at 1273 K for 15 h in an alumina crucible using a tube furnace. The calcined materials were washed with deionized water three times to remove the residual NaCl flux.

2.2.2. Preparation of NaTaO₃ photocatalyst

NaTaO₃ was synthesized by the solid-state reaction method. Na₂CO₃, NaCl and Ta₂O₅ as starting materials were mixed in an agate mortar in a ratio of Na: Ta = 1: 1. And the ratio of Na₂CO₃ and NaCl was 0.5: 1. The mixture was calcined in air at 1273 K for 15 h in an alumina crucible using a tube furnace.

2.2.3. Preparation of Ag_xNa_{1-x}TaO₃ photocatalyst

Ag_xNa_{1-x}TaO₃ was synthesized by the solid-state reaction method. Na₂CO₃, Ta₂O₅, and Ag₂O as starting materials were mixed in an agate mortar in a ratio of Na: Ta: Ag = 1.05: 2: 1. The mixture was calcined in air at 1273 K for 15 h in an alumina crucible using a tube furnace.

2.2.4. Preparation of NaTaO₃-AgCl photocatalyst

NaTaO₃ nanoparticles were synthesized by the solid-state reaction method. Then a certain amount (a ratio of Na: Ag = 1: 1) of AgNO₃ aqueous solution was added to the beaker and finally added excessive amounts of HCl aqueous solution with magnetic stirring for 2 h. It was denoted as NaTaO₃-AgCl.

2.2.5. Modification of photocatalyst with Ag cocatalyst

Ag cocatalyst was loaded by liquid-phase chemical reduction, impregnation, and photodeposition using AgNO₃ as the precursors. In the liquid-phase chemical reduction method, an aqueous AgNO₃ solution was added to a suspension containing the photocatalyst. After the

addition of aqueous NaPH₂O₂ solution as a reducing reagent to the suspension, the mixture was stirred at 363 K for 2 h. The Ag-impregnated photocatalyst was reduced by H₂ gas at 473 K for 1 h to obtain metallic Ag cocatalyst. The Ag cocatalyst was also loaded by *in-situ* photodeposition using AgNO₃ as the precursors. For comparison, Ag-modified Ag_xNa_{1-x}TaO₃-AgCl composites with different loading amounts (1 wt%, 2 wt%, 3 wt%, 4 wt%, and 5 wt%) of Ag were prepared under identical conditions.

2.3. Characterization of photocatalysts

X-ray diffraction (XRD) was carried out using a Bruker, D8A A25 powder diffractometer equipped with a Cu K α (λ = 0.154056 nm) radiation source and using a voltage and current of 40 kV and 40 mA, respectively. X-ray photoelectron spectroscopy (XPS) measurement was implemented on a Thermo Scientific ESCALAB 250Xi spectrometer with a monochromatic Al K α source ($h\nu$ = 1486.6 eV) and normalized to C 1 s for each sample. Sputter-etching is performed using an ion beam with 4 keV Ar ions incident at an angle of 40°. The sputtering rates obtained using the reference Ta₂O₅ sample are 0.82 nm/s. The area of the ion beam is over 1 mm², while the area analyzed by XPS is 0.2 mm² and located in the center of the ion-etched region. Scanning electron microscopy images were taken using a field-emission scanning electron microscope (HITACHI, SU8020). High-resolution transmission electron microscope images were obtained using a JEM-2100Plus electron microscope operated at 200 kV. UV-vis diffuse reflectance spectroscopy (UV-vis DRS) was performed using a Perkin Elmer Lambda 650 S spectrometer equipped with an integrating sphere. A physisorption analyzer (Micromeritics, ASAP 2020 M) was used to obtain the specific surface area. The catalysts were degassed at 473 K for 6 h before measurement.

CO₂-TPD experiments were carried out on a Nicolet IS50 spectrometer (Thermo, Beijing, China) with an MCT/A detector. Each sample (100 mg) with a quartz U-tube reactor was heated under ultra-high purity N₂ flow (30 mL·min⁻¹) up to 673 K at 283 K·min⁻¹ for 1 h and then it was cooled to room temperature. After pretreatment, 10% CO₂ flow (total flow rate of CO₂/N₂ gases: 30 mL·min⁻¹) passed through the catalyst bed for 30 min, subsequently, the sample was flushed by N₂ flow (30 mL·min⁻¹) for 60 min. Then, the TPD analysis was performed under N₂ flow (30 mL·min⁻¹) by heating the sample at a rate of 10 K·min⁻¹ up to 673 K. The calibration curve of the amount of CO₂ was made by the decomposition of (NH₄)₂CO₃ under the same testing conditions, and the amount of CO₂ adsorbed on the sample was calculated based on this calibration curve.

2.4. Photoelectrochemical measurements

Electrochemical measurements were performed by using a CHI 650E electrochemical workstation with a standard three-electrode cell at room temperature. The prepared sample, an Ag/AgCl electrode (saturated KCl), and a Pt wire are used as the working electrode, the reference electrode, and the counter electrode, respectively. The preparation of working electrodes refers to the literature reported. A fluorine-doped tin oxide (FTO) glass piece with a size of 1 × 1 cm was sonicated in acetone and absolute ethanol, and then rinsed with deionized water and dried in an air stream. A suspension of 100 mg of the powder in 2 mL of absolute ethanol was used for casting onto the FTO glass substrate. The coated glass was then heated at 473 K in the air for 1 h to improve adhesion. The electrochemical impedance spectroscopy (EIS) was recorded by applying an AC voltage of 10 mV amplitude in the frequency range of 10⁵ Hz to 10 Hz with the initial potential (0 V) in 0.1 M Na₂SO₄. For photocurrent measurement, a 300 W Xe arc lamp served as a light source and Na₂SO₄ (0.1 M) aqueous solution was used as the electrolyte.

To estimate the conduction band potential (E_{CB}), the flat-band potential (E_f) of the samples was calculated by the Mott-Schottky equation. For n-type semiconductors, $E_{CB} = E_f - 0.2$ V. Use the formula to

calculate the band gap (E_g) = $1240/\lambda_g$ (eV). The valence band potential (E_{VB}) can be calculated according to the following formula: $E_{VB} = \varphi + E_{VB, XPS} - 4.44$, where φ is the work function of the instrument (4.66 eV). Finally, the band gap relationship of different samples conforms to the empirical formula: $E_g = E_{VB} - E_{CB}$.

2.5. Photocatalytic CO₂ reduction test

Photocatalytic reactions were carried out in a gas-flow system using a top-irradiation cell equipped with a 300 W Xe lamp as a light source. The 0.3 g photocatalyst powder was dispersed in 100 mL of water. Ar gas (99.999%) was continuously introduced into the reactor before the reaction to remove the air. Photocatalytic reactions were carried out by flowing the CO₂/Ar mixed gas with a total rate of 30 mL·min⁻¹. The concentration of CO₂ in CO₂/Ar mixed gas was controlled by adjusting the flow rates of CO₂ gas (99.9997%) and Ar gas (99.999%). The reaction system was connected to the cooling water system to maintain the reactor at room temperature. Gaseous products were determined by online gas chromatographs (Shimadzu, GC-2014) with a thermal conductivity detector (MS-13X, Ar carrier) and a flame ionization detector (SC-ST, N₂ carrier) with a methanizer.

3. Results and discussion

3.1. Characterization of Ag_xNa_{1-x}TaO₃-AgCl heterojunction photocatalyst

The crystal structure of Ag_xNa_{1-x}TaO₃-AgCl heterojunction photocatalyst was first analyzed. Fig. 1 shows XRD patterns of the obtained Ag_xNa_{1-x}TaO₃-AgCl, Ag_xNa_{1-x}TaO₃, NaTaO₃-AgCl and NaTaO₃ samples. NaTaO₃ synthesized by the solid-state reaction method was pure phase according to the standard XRD pattern of JCPDS card No. 73-0878. Ag_xNa_{1-x}TaO₃ sample exhibited the same XRD peaks of NaTaO₃ without any impurity phase, whereas Ag_xNa_{1-x}TaO₃-AgCl and NaTaO₃-AgCl samples had the main phase of NaTaO₃ together with the appearance of typical XRD peaks corresponding to AgCl (JCPDS NO. 85-1355), suggesting the formation of heterostructure composite. The intensities of XRD peaks assigned to NaTaO₃ phase and AgCl phase in Ag_xNa_{1-x}TaO₃-AgCl composite were obviously higher than those in NaTaO₃ by solid-state reaction method and NaTaO₃-AgCl with twofold AgCl weight ratio, indicating that highly-crystalline Ag_xNa_{1-x}TaO₃-AgCl composite was successfully grown in the one-step flux synthesis process. Moreover, the XRD peak positions of Ag_xNa_{1-x}TaO₃-AgCl and Ag_xNa_{1-x}TaO₃ samples shifted to smaller diffraction angle as compared with pure NaTaO₃, which implied Na⁺ cations at the A sites of perovskite NaTaO₃ crystal structure were replaced by Ag⁺ cations having the

slightly larger ionic radius. Considering the pure phase of the Ag_xNa_{1-x}TaO₃ sample, the Ag_xNa_{1-x}TaO₃ component in the Ag_xNa_{1-x}TaO₃-AgCl composite was a solid solution. As a result, Ag_xNa_{1-x}TaO₃-AgCl heterostructure photocatalyst with high crystallinity and homogeneous Ag incorporation was synthesized via the one-step flux method.

To investigate the chemical components from the surface to the interior of Ag_xNa_{1-x}TaO₃-AgCl, the depth analysis of XPS was carried out using Ar ion etching. Fig. 2 shows XPS spectra of the Ag_xNa_{1-x}TaO₃-AgCl composite acquired at the interval of Ar sputtering for 30.9 s and the elemental ratio at each step of Ar ion sputter-etching. The Ag 3d peaks of Ag_xNa_{1-x}TaO₃-AgCl in 61.8 s of Ar sputtering were mainly located at 373.1 and 367.1 eV (Fig. 2a), which were attributed to AgCl species. After Ar ion etching for 92.7 s, the locations of Ag 3d peaks shifted to 373.8 and 367.8 eV assigned to the binding energy between Ag cations and O anions, then were kept at the same position. In addition, the chemical states of Cl, Na, Ta, and O ions respectively remained unchanged (Fig. 2b-e). The elemental ratios from the surface to the interior of the Ag_xNa_{1-x}TaO₃-AgCl composite were estimated according to the areas of XPS peaks at each step of Ar sputtering. As shown in Fig. 2f, the amount of Cl element decreased with the increase of Ar etching time and was negligible after 92.7 s etching, related to the binding energy change of Ag element. Simultaneously, the concentrations of Ag, Na, Ta, and O ions in the Ag_xNa_{1-x}TaO₃-AgCl composite reached the steady ratio of 1: 1: 2: 6 after Ar sputtering for 92.7 s (Fig. 2f). Therefore, it is demonstrated that AgCl phase was grown on the surface of Ag_xNa_{1-x}TaO₃ phase to form the intimate heterojunction in Ag_xNa_{1-x}TaO₃-AgCl composite and Ag cations were incorporated into NaTaO₃ structure as Ag_{0.5}Na_{0.5}TaO₃.

The morphology and interface structure of Ag_xNa_{1-x}TaO₃-AgCl heterojunction photocatalyst were investigated by SEM and TEM as shown in Fig. 3 and Fig. S1. In contrast to the cube-like shape of pristine NaTaO₃ with a clean surface (Fig. 3b), Ag_xNa_{1-x}TaO₃-AgCl composite by the one-step flux method exhibited the enlarged cuboid Ag_xNa_{1-x}TaO₃ particles with the aggregated small AgCl grains on the surface (Fig. 3a), which agreed well with high crystallinity and heterostructure of Ag_xNa_{1-x}TaO₃-AgCl reflected from XRD and XPS results. Moreover, the HRTEM images of the Ag_xNa_{1-x}TaO₃-AgCl composite (Fig. S1) showed the clear lattice fringes related to Ag_xNa_{1-x}TaO₃ and AgCl components and the intimate contact at the interface between the two phases. It is expected that the heterojunction structure in high-crystalline Ag_xNa_{1-x}TaO₃-AgCl photocatalyst will enable the efficient charge separation and migration to promote the conversion of CO₂ in H₂O.

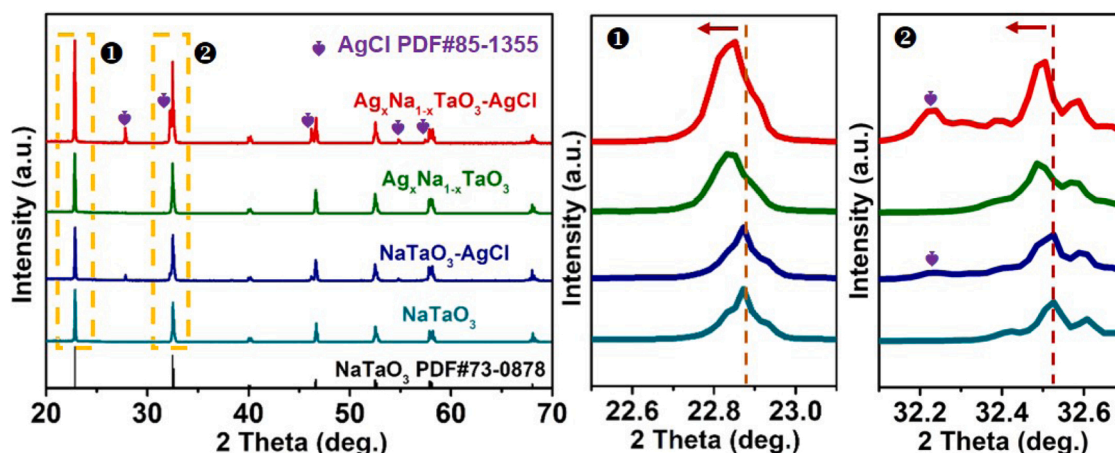


Fig. 1. XRD patterns of Ag_xNa_{1-x}TaO₃-AgCl, Ag_xNa_{1-x}TaO₃, NaTaO₃-AgCl and NaTaO₃ samples.

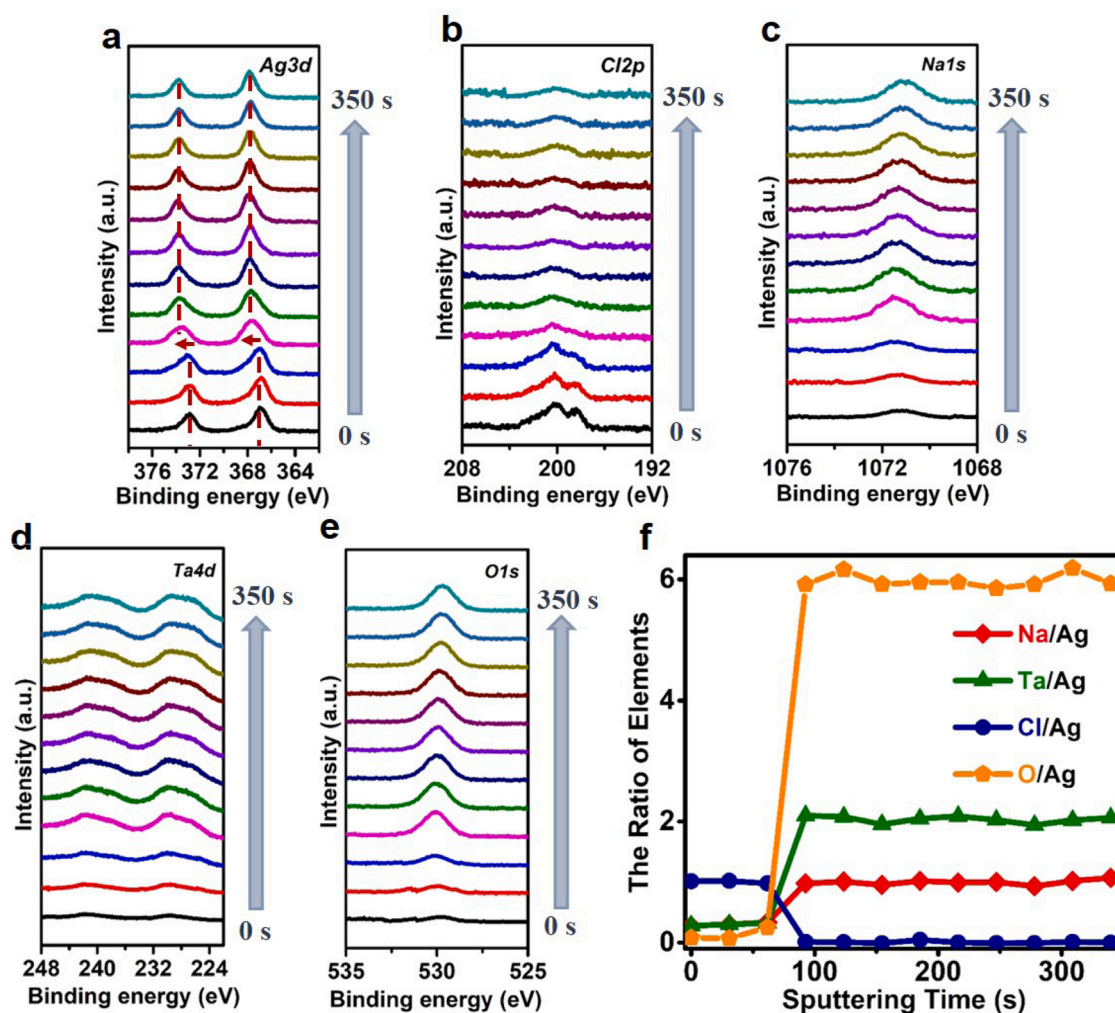


Fig. 2. XPS spectra of (a) Ag 3d, (b) Cl 2p, (c) Na 1 s, (d) Ta 4d, (e) O 1 s, and (f) the atomic ratio of each element for $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ during Ar ion etching.

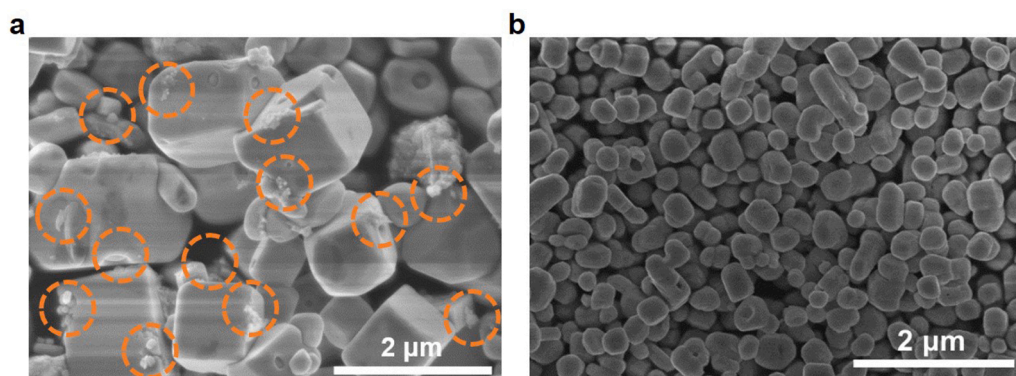


Fig. 3. SEM images of (a) $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ and (b) pristine NaTaO_3 samples. The $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ was synthesized by the one-step flux method. The pristine NaTaO_3 was synthesized by the solid-state reaction method.

3.2. Band structure and charge separation of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ photocatalyst

To further confirm the formation of heterojunction structure, the bandgap energy and band positions of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ and AgCl components in $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ were characterized by UV-vis DRS and Mott-Schottky plots. Fig. 4a-b display that the as-synthesized NaTaO_3 , $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ and AgCl had the light absorption edges at 303 nm,

308 nm and 405 nm, corresponding to the band gap of 4.10 eV, 4.03 eV and 3.06 eV, respectively. Owing to the incorporation of Ag cations into the NaTaO_3 matrix and the combination with AgCl, the $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ heterostructure photocatalyst exhibited a red shift of the absorption edge. The absorption background of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ were higher than that of NaTaO_3 due to the plasmon resonance effect of AgCl component and Ag incorporation. Moreover, the relative band potentials of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ and AgCl components in the $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$

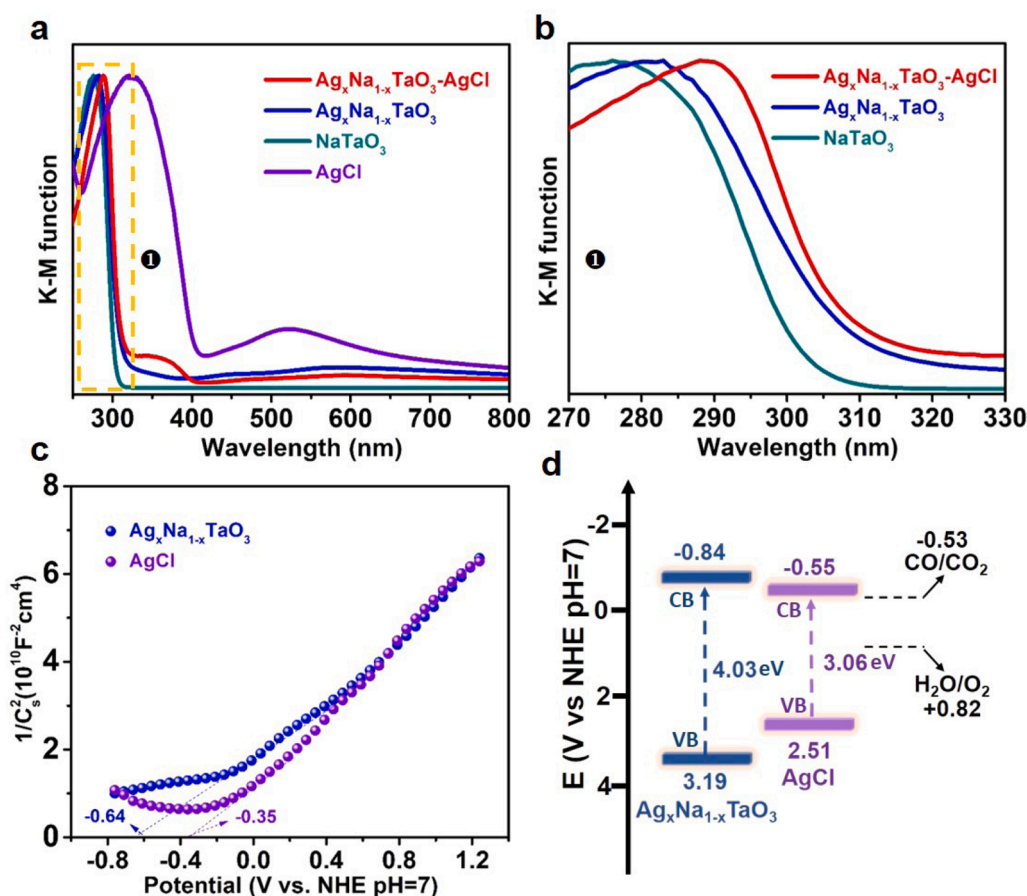


Fig. 4. (a-b) UV-vis DRS of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$, $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$, NaTaO_3 and AgCl , (c) Mott-Schottky plots of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ and AgCl , (d) the relative band positions of the $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ heterostructure.

composite were evaluated according to Mott-Schottky plots. In Fig. 4c, the flat-band potentials of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ and AgCl were fitted to be around -0.64 V and -0.35 V vs. NHE (pH 7), respectively. Considering that the bottom of the conduction band (CB) for n-type semiconductors (Mott-Schottky plots with positive slope) generally locates at about 0.2 V more negative potential than the flat band potential [38], the CB minimum positions of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ and AgCl were determined to be -0.84 V and -0.55 V, respectively. Moreover, the valence band (VB) maximum positions of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ and AgCl were acquired by XPS valence band spectra (Fig. S2), which is consistent with the estimation

from Mott-Schottky plots and the bandgap. In combination with these results, the band alignment of two components in $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ heterojunction photocatalyst was proposed in Fig. 4d. A typical type I heterojunction was formed in $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ photocatalyst, where CB and VB of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ component straddled those of AgCl component. Therefore, the transfer of photogenerated electrons from $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ to AgCl in $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ heterojunction photocatalyst is thermodynamically feasible, leading to the efficient charge separation.

The effect of the heterojunction of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ photocatalyst

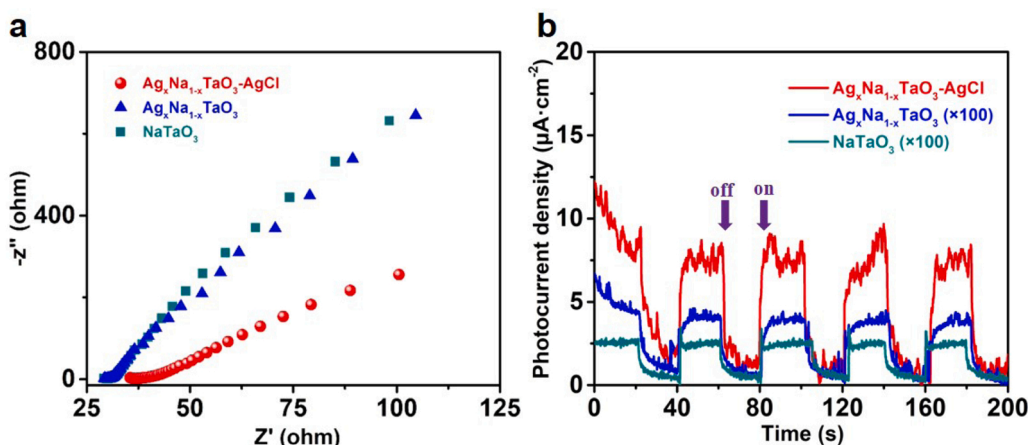


Fig. 5. (a) EIS Nyquist plots and (b) photocurrent density of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$, $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ and NaTaO_3 .

on the separation efficiency of photogenerated electron-hole pairs was investigated by EIS and photocurrent measurements. Fig. 5a shows EIS Nyquist plots of NaTaO_3 , $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ and $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ photocatalysts. As compared with pristine NaTaO_3 , the slight decrease in the arc size of the EIS curve for $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ photocatalyst indicates that Ag incorporation helped to reduce the charge-transfer resistance. Obviously, the $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ photocatalyst possessed the smallest resistance enabling fast separation and transfer of photogenerated charges. As a result, the photocurrent density of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ was 145 times and 230 times higher than that of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ and NaTaO_3 (Fig. 5b), respectively. The above results specifically confirm that efficient charge separation and transfer is readily available on the high-crystalline $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ heterojunction structure towards photocatalytic CO_2 conversion with H_2O oxidation.

3.3. Photocatalytic conversion of low-concentration CO_2

In the photocatalytic CO_2 reduction by H_2O , high-concentration CO_2 gas is generally introduced into an alkaline solution for the improvement of CO_2 solubility and CO_2 mass transfer in the photocatalytic system [38–40]. To our knowledge, the production of high-concentration CO_2 feedstock through the CO_2 capture and purification process will demand more energy input for the practical application of CO_2 conversion. Therefore, it is highly desirable to promote the performance for photocatalytic conversion of low-concentration CO_2 with H_2O oxidation. The CO_2 reduction reaction over the $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ heterojunction photocatalyst was carried out in pure H_2O with low-concentration CO_2 flow under UV light irradiation. Fig. 6a shows the effect of different CO_2 concentrations on the photocatalytic activity of CO_2 conversion over bare $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$. CO gas as the reduction product and O_2 gas as the oxidation product were simultaneously evolved, indicating that H_2O functioned as the electron donor for photocatalytic CO_2 conversion. The selectivity towards CO_2 reduction on the $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ photocatalyst was 100%. It is worth noting that the photocatalytic activity for CO_2 reduction with H_2O oxidation gradually decreased with the increase of CO_2 feeding concentration from 10% to 100%. It has been well-known that Ag cocatalyst can act as the active site for photocatalytic conversion of CO_2 to produce CO, due to the moderate binding of Ag atom and CO molecule rendering smooth desorption of CO from Ag particle surface [41]. Therefore, when metallic Ag nanoparticles were uniformly dispersed on $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ which was confirmed by HRTEM and XPS (Fig. S3), the photocatalytic performance for CO_2 reduction with H_2O oxidation over

the heterojunction photocatalyst was dramatically enhanced at various CO_2 concentrations (Fig. 6b). The Ag-modified $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ photocatalyst exhibited superior activity at 10% CO_2 feeding condition as well, and about 7.6 times higher evolution rate of CO than bare $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ photocatalyst. Additionally, the effects of the different loading methods and loading amounts of metallic Ag cocatalyst on the photocatalytic conversion of low-concentration CO_2 were shown in Table S1. The optimal photocatalytic activity over $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ was obtained when 2 wt% metallic Ag cocatalyst was loaded by liquid-phase chemical reduction method. These results clearly demonstrate the validity of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ heterojunction photocatalyst for the low-concentration CO_2 conversion.

The activities of different NaTaO_3 -based photocatalysts loaded with metallic Ag nanoparticle cocatalyst at low-concentration CO_2 were compared as shown in Fig. 7a-b. The evolution rates of CO from CO_2 conversion on $\text{NaTaO}_3\text{-AgCl}$ and $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ photocatalysts were much higher than that on NaTaO_3 photocatalyst, implying that the formation of heterostructure with AgCl and the incorporation of Ag into NaTaO_3 crystal lattice both contributed to the activity enhancement. The optimal ratio between Na and Ag in $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ solid solution (Table S2) was consistent with that in $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ component of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ heterostructure. The $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ heterojunction photocatalyst prepared via the high-temperature one-step flux method exhibited the increased crystallinity of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ and AgCl and the enhanced interfacial contact between these two components, so that the photocatalytic activity for low-concentration CO_2 conversion was promoted to the level at least 20-fold higher than that of other three photocatalysts. Simultaneously, O_2 was steadily evolved over Ag-modified $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ during photocatalytic CO_2 conversion as shown in Fig. S4, and Ag-modified $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ photocatalyst was unchangeable before and after CO_2 conversion reaction confirmed by SEM images and XRD patterns (Fig. S5). Furthermore, the photocatalytic CO_2 reduction performance correlated well with the CO_2 adsorption capacities of four photocatalysts, increased in the order of NaTaO_3 , $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$, $\text{NaTaO}_3\text{-AgCl}$ and $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ regardless of the similar specific surface areas (Fig. 7c and Table S3-4). As a result, the high-crystalline $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ heterojunction structure afforded the fast separation and transfer of photogenerated charges, and the combination of $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3$ and AgCl components allowed the strengthened chemisorption and activation of CO_2 molecules. Both of these two aspects integrally overcame the condition of low mass transfer and exchange, thus facilitating the photocatalytic conversion of low-concentration CO_2 with H_2O oxidation over

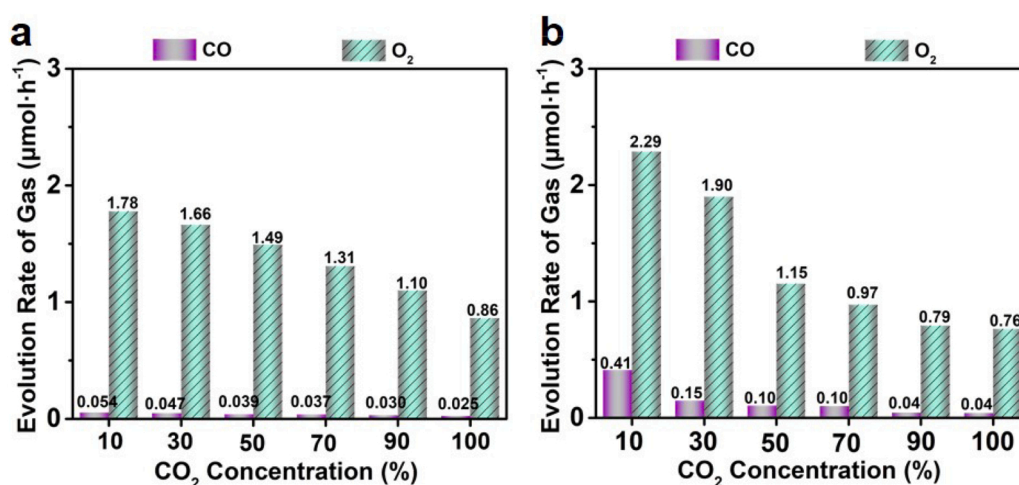


Fig. 6. Evolution rates of CO and O_2 over (a) bare $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ photocatalyst and (b) Ag-modified $\text{Ag}_x\text{Na}_{1-x}\text{TaO}_3\text{-AgCl}$ photocatalyst at different CO_2 concentrations; Photocatalyst: 0.3 g; cocatalyst: 2 wt% of Ag by a liquid phase reduction method; reactant solution: 100 mL pure water; CO_2/Ar gas flow rate: 30 mL·min⁻¹; light Source: 300 W Xe-lamp.

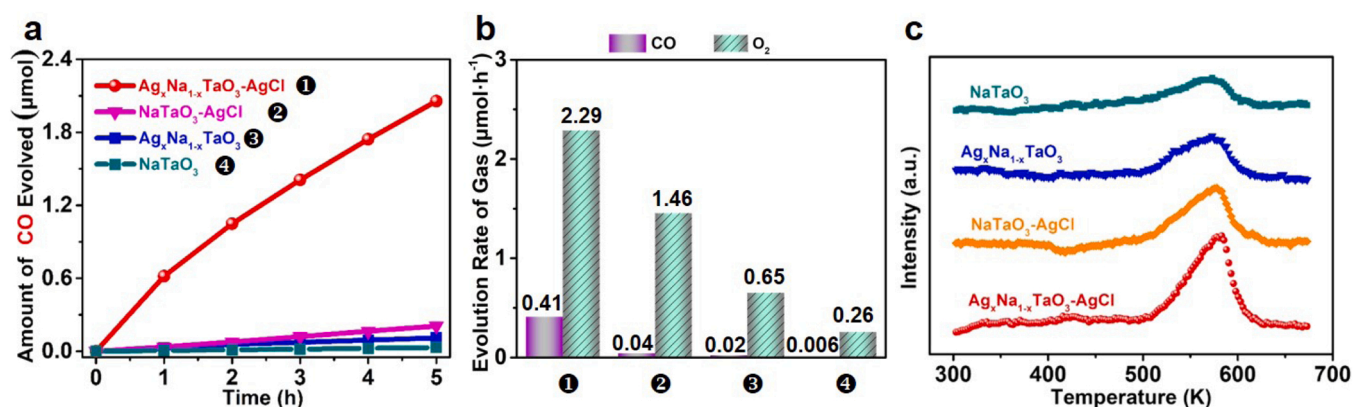


Fig. 7. (a) The amount of CO evolution and (b) Evolution rate of CO and O₂ over Ag-modified Ag_xNa_{1-x}TaO₃-AgCl, Ag-modified NaTaO₃-AgCl, Ag-modified Ag_xNa_{1-x}TaO₃ and Ag-modified NaTaO₃ at 10% CO₂ concentration. Photocatalyst: 0.3 g; cocatalyst: 2 wt% of Ag by a liquid phase reduction method; reactant solution: 100 mL pure water; CO₂/Ar gas flow rate: 30 mL·min⁻¹; light Source: 300 W Xe-lamp; (c) CO₂-TPD profiles for Ag_xNa_{1-x}TaO₃-AgCl, NaTaO₃-AgCl, Ag_xNa_{1-x}TaO₃ and NaTaO₃ samples.

Ag_xNa_{1-x}TaO₃-AgCl photocatalyst. In addition, most of photocatalysts for low-concentration CO₂ conversion in the literatures (Table S5) were either synthesized in a complicated process or functioned in the system containing sacrificial reagent. Our Ag_xNa_{1-x}TaO₃-AgCl heterojunction photocatalyst fabricated by a facile one-step flux method had the advantages in low-concentration CO₂ conversion using H₂O as electron donor. Nevertheless, the conversion efficiency of low-concentration CO₂ on Ag_xNa_{1-x}TaO₃-AgCl heterojunction photocatalyst are necessary to be further improved.

4. Conclusion

The Ag_xNa_{1-x}TaO₃-AgCl photocatalyst with the high-crystalline heterojunction structure has been successfully fabricated via a one-step flux method. The *in-situ* combination of Ag_xNa_{1-x}TaO₃ and AgCl components at high temperature made a strong interaction at the junction interface, so the matched band positions and the decreased recombination centers in Ag_xNa_{1-x}TaO₃-AgCl heterostructure encouraged the separation and transfer efficiency of photogenerated electron-hole pairs. In addition, the presence of surface Ag cations in Ag_xNa_{1-x}TaO₃ and AgCl particles on Ag_xNa_{1-x}TaO₃ greatly enforced CO₂ adsorption capability. Upon the modification with metallic Ag nanoparticles as the active reduction cocatalyst, the high-crystalline Ag_xNa_{1-x}TaO₃-AgCl heterostructure gave the remarkably improved photocatalytic activity for the conversion of low-concentration CO₂ with H₂O oxidation. Accordingly, this study provided an effective method for the development of heterojunction photocatalysts achieving efficient solar-to-chemical energy conversion.

CRediT authorship contribution statement

Qiaoqi Guo: Investigation, Formal analysis, Data curation, Writing - original draft, Writing - review & editing. **Ying Luo:** Investigation, Formal analysis, Data curation, Methodology, Validation. **Jun Xu:** Formal analysis, Data curation, Methodology, Writing - review & editing. **Lidan Deng:** Writing - review & editing, Validation. **Zheng Wang:** Conceptualization, Methodology, Validation, Writing - review & editing, Project administration, Resources, Supervision. **Hong He:** Conceptualization, Writing - review & editing, Project administration, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2022.122253.

References

- [1] A.A. Lacis, G.A. Schmidt, D. Rind, R.A. Ruedy, Atmospheric CO₂: principal control knob governing earth's temperature, *Science* 330 (2010) 356–359.
- [2] W.R. Peltier, A. Tushingham, Global sea level rise and the greenhouse effect: might they be connected? *Science* 244 (1989) 806–810.
- [3] Y. He, L. Zhang, B. Teng, M. Fan, New application of Z-scheme Ag₃PO₄/g-C₃N₄ composite in converting CO₂ to fuel, *Environ. Sci. Technol.* 49 (2015) 649–656.
- [4] W. Zhang, D. Ma, J. Pérez-Ramírez, Z. Chen, Recent progress in materials exploration for thermocatalytic, photocatalytic, and integrated photothermocatalytic CO₂-to-fuel conversion, *Adv. Energy Sustain. Res.* 3 (2022), 2100169.
- [5] T. Wilberforce, A. Olabi, E.T. Sayed, K. Elsaid, M.A. Abdelkareem, Progress in carbon capture technologies, *Sci. Total Environ.* 761 (2021), 143203.
- [6] P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber, T.E. Müller, Worldwide innovations in the development of carbon capture technologies and the utilization of CO₂, *Energy Environ. Sci.* 5 (2012) 7281–7305.
- [7] Y.H. Yan, T. Borhani, G. Subraveti, N. Pai, V. Prasad, A. Rajendran, P. Nkulikiyinka, J.O. Asibor, Z. Zhang, D. Shao, Harnessing the power of machine learning for carbon capture, utilisation, and storage (CCUS)-a state-of-the-art review, *Energy Environ. Sci.* 14 (2021) 6122–6157.
- [8] Z. Zhang, T. Wang, M.J. Blunt, E.J. Anthony, A.-H.A. Park, R.W. Hughes, P. A. Webley, J. Yan, Advances in carbon capture, utilization and storage, *Appl. Energy* 278 (2020), 115627.
- [9] G. Zhang, G. Liu, L. Wang, J.T. Irvine, Inorganic perovskite photocatalysts for solar energy utilization, *Chem. Soc. Rev.* 45 (2016) 5951–5984.
- [10] J. Ran, M. Jaroniec, S.Z. Qiao, Cocatalysts in semiconductor-based photocatalytic CO₂ reduction: achievements, challenges, and opportunities, *Adv. Mater.* 30 (2018), 1704649.
- [11] H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu, X. Wang, Semiconductor heterojunction photocatalysts: design, construction, and photocatalytic performances, *Chem. Soc. Rev.* 43 (2014) 5234–5244.

- [12] J.L. DiMeglio, J. Rosenthal, Selective conversion of CO₂ to CO with high efficiency using an inexpensive bismuth-based electrocatalyst, *J. Am. Chem. Soc.* 135 (2013) 8798–8801.
- [13] Y. Chen, C.W. Li, M.W. Kanan, Aqueous CO₂ reduction at very low overpotential on oxide-derived Au nanoparticles, *J. Am. Chem. Soc.* 134 (2012) 19969–19972.
- [14] S. Cao, B. Shen, T. Tong, J. Fu, J. Yu, 2D/2D heterojunction of ultrathin MXene/Bi₂WO₆ nanosheets for improved photocatalytic CO₂ reduction, *Adv. Funct. Mater.* 28 (2018), 1800136.
- [15] Z. Wang, K. Teramura, S. Hosokawa, T. Tanaka, Highly efficient photocatalytic conversion of CO₂ into solid CO using H₂O as a reductant over Ag-modified ZnGa₂O₄, *J. Mater. Chem. A* 3 (2015) 11313–11319.
- [16] Z. Wang, K. Teramura, S. Hosokawa, T. Tanaka, Photocatalytic conversion of CO₂ in water over Ag-modified La₂Ti₂O₇, *Appl. Catal. B Environ.* 163 (2015) 241–247.
- [17] S. Yan, J. Wang, H. Gao, N. Wang, H. Yu, Z. Li, Y. Zhou, Z. Zou, Zinc gallogermanate solid solution: a novel photocatalyst for efficiently converting CO₂ into solar fuels, *Adv. Funct. Mater.* 23 (2013) 1839–1845.
- [18] K. Iizuka, T. Wato, Y. Miseki, K. Saito, A. Kudo, Photocatalytic reduction of carbon dioxide over Ag cocatalyst-loaded Al_{0.4}Ti₄O₁₅ (A = Ca, Sr, and Ba) using water as a reducing reagent, *J. Am. Chem. Soc.* 133 (2011) 20863–20868.
- [19] S. Yan, L. Wan, Z. Li, Z. Zou, Facile temperature-controlled synthesis of hexagonal Zn₂GeO₄ nanorods with different aspect ratios toward improved photocatalytic activity for overall water splitting and photoreduction of CO₂, *Chem. Commun.* 47 (2011) 5632–5634.
- [20] R. Ito, M. Akatsuka, A. Ozawa, Y. Kato, Y. Kawaguchi, M. Yamamoto, T. Tanabe, T. Yoshida, Photocatalytic activity of Ga₂O₃ supported on Al₂O₃ for water splitting and CO₂ reduction, *ACS Omega* 4 (2019) 5451–5458.
- [21] T. Takayama, A. Iwase, A. Kudo, Photocatalytic water splitting and CO₂ reduction over KCaSrTa₅O₁₅ nanorod prepared by a polymerized complex method, *Bull. Chem. Soc. Jpn.* 88 (2015) 538–543.
- [22] H. Nakanishi, K. Iizuka, T. Takayama, A. Iwase, A. Kudo, Highly active NaTaO₃-based photocatalysts for CO₂ reduction to form CO using water as the electron donor, *ChemSusChem* 10 (2017) 112–118.
- [23] Q. Guo, J. Xu, Y. Luo, Y. Yang, Z. Wang, H. He, Cocatalyst modification of AgTaO₃ photocatalyst for conversion of carbon dioxide with water, *J. Phys. Chem. C* 125 (2021) 26389–26397.
- [24] X. Wu, Y. Li, G. Zhang, H. Chen, J. Li, K. Wang, Y. Pan, Y. Zhao, Y. Sun, Y. Xie, Photocatalytic CO₂ conversion of Mo_{0.33}WO₃ directly from the air with high selectivity: insight into full spectrum-induced reaction mechanism, *J. Am. Chem. Soc.* 141 (2019) 5267–5274.
- [25] S. You, S. Guo, X. Zhao, M. Sun, C. Sun, Z. Su, X. Wang, All-inorganic perovskite/graphitic carbon nitride composites for CO₂ photoreduction into C1 compounds under low concentrations of CO₂, *Dalton Trans.* 48 (2019) 14115–14121.
- [26] Z. Wang, C. Li, K. Domen, Recent developments in heterogeneous photocatalysts for solar-driven overall water splitting, *Chem. Soc. Rev.* 48 (2019) 2109–2125.
- [27] E. Grabowska, Selected perovskite oxides: characterization, preparation and photocatalytic properties—a review, *Appl. Catal. B Environ.* 186 (2016) 97–126.
- [28] H. Kato, K. Asakura, A. Kudo, Highly efficient water splitting into H₂ and O₂ over lanthanum-doped NaTaO₃ photocatalysts with high crystallinity and surface nanostructure, *J. Am. Chem. Soc.* 125 (2003) 3082–3089.
- [29] G.R. Portugal, S.F. Santos, J.T. Arantes, NaTaO₃ cubic and orthorhombic surfaces: an intrinsic improvement of photocatalytic properties, *Appl. Surf. Sci.* 502 (2020), 144206.
- [30] V. Jeyalakshmi, R. Mahalakshmy, K. Ramesh, P.V. Rao, N.V. Choudary, K. Thirunavukkarasu, K.R. Krishnamurthy, B. Viswanathan, Metal oxides as photocatalysts: modified sodium tantalate as catalyst for photoreduction of carbon dioxide, *Mol. Catal.* 451 (2018) 105–113.
- [31] L. An, H. Onishi, Electron-hole recombination controlled by metal doping sites in NaTaO₃ photocatalysts, *ACS Catal.* 5 (2015) 3196–3206.
- [32] H. Sudrajat, S. Babel, I. Thushari, K. Laohhasurayotin, Stability of La dopants in NaTaO₃ photocatalysts, *J. Alloy. Compd.* 775 (2019) 1277–1285.
- [33] H. Li, X. Shi, X. Liu, X. Li, Synthesis of novel, visible-light driven S, N-doped NaTaO₃ catalysts with high photocatalytic activity, *Appl. Surf. Sci.* 508 (2020), 145306.
- [34] J. Mora-Hernandez, A.M. Huerta-Flores, L.M. Torres-Martinez, Photoelectrocatalytic characterization of carbon-doped NaTaO₃ applied in the photoreduction of CO₂ towards the formaldehyde production, *J. CO₂ Util.* 27 (2018) 179–187.
- [35] X. Wang, J. Ma, Y. Kong, C. Fan, M. Peng, S. Komarneni, Synthesis of p-n heterojunction Ag₃PO₄/NaTaO₃ composite photocatalyst for enhanced visible-light-driven photocatalytic performance, *Mater. Lett.* 251 (2019) 192–195.
- [36] S. Yang, D. Xu, B. Chen, B. Luo, X. Yan, L. Xiao, W. Shi, Synthesis and visible-light-driven photocatalytic activity of p-n heterojunction Ag₂O/NaTaO₃ nanocubes, *Appl. Surf. Sci.* 383 (2016) 214–221.
- [37] G.Z. Wang, H. Chen, X.K. Luo, H.K. Yuan, A.L. Kuang, Bandgap engineering of SrTiO₃/NaTaO₃ heterojunction for visible light photocatalysis, *Int. J. Quantum Chem.* 117 (2017), e25424.
- [38] Y. Qi, S. Chen, M. Li, Q. Ding, Z. Li, J. Cui, B. Dong, F. Zhang, C. Li, Achievement of visible-light-driven Z-scheme overall water splitting using barium-modified Ta₃N₅ as a H₂-evolving photocatalyst, *Chem. Sci.* 8 (2017) 437–443.
- [39] S. Wang, K. Teramura, T. Hisatomi, K. Domen, H. Asakura, S. Hosokawa, T. Tanaka, Effective driving of Ag-loaded and Al-doped SrTiO₃ under irradiation at λ > 300 nm for the photocatalytic conversion of CO₂ by H₂O, *ACS Appl. Energy Mater.* 3 (2020) 1468–1475.
- [40] R. Pang, K. Teramura, H. Asakura, S. Hosokawa, T. Tanaka, Effect of Cr species on photocatalytic stability during the conversion of CO₂ by H₂O, *J. Phys. Chem. C* 123 (2019) 2894–2899.
- [41] M. Yamamoto, T. Yoshida, N. Yamamoto, T. Nomoto, Y. Yamamoto, S. Yagi, H. Yoshida, Photocatalytic reduction of CO₂ with water promoted by Ag clusters in Ag/Ga₂O₃ photocatalysts, *J. Mater. Chem. A* 3 (2015) 16810–16816.